7 Update Report on nPB

In Decision XIII/7, Parties requested an annual update on the evolution of use and emissions of n-propyl bromide; this report provides the most recent available data.

7.1 Market factors

Owing to the uncertain toxicity and probable environmental restrictions on the use of nPB and the economic conditions, the market for nPB for solvents use has not developed significantly in most countries, since the publication of the 2002 Update Report (TEAP, 2002). A number of companies have avoided making capital investments for the safe use of nPB, pending the outcome of the geopolitical situation and the consequent economic effects. There may be a significant market expansion in China, although no figures have been reported[28].

There has been an increase reported in the use of nPB as a cold cleaning solvent in Western Europe (Rollet, 2003). This application is emissive.

The price of nPB has dropped and typical bulk prices in Europe and North America are between USD 1.70 and 1.80 per kilogram, probably due to increased global production capacity. This nPB price overlaps the higher end of the chlorinated solvent price range. In countries where the regulatory restrictions on the use of nPB are less onerous than those for chlorinated solvents a significant increase in future use may occur.

7.2 Regulatory Influences

Proposed regulations in the EU and USA would restrict potential use within these jurisdictions and may discourage use elsewhere.

The proposed EU Classification and Labelling Requirements, shown in updated Table 7-1 (mentioned as a proposal in the 2002 Update Report) are now scheduled for voting in mid-2003 and expected to enter into force in mid-2004.

TEAP has identified no major new proposed or promulgated regulations, pending the outcome of scientific toxicological and environmental studies.

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[28] Decision 33/46 of the Executive Committee of the Multilateral Fund calls for nPB reporting and it is thought that the UNDP will make the first report in July 2003 at the 40th meeting of the committee.

The US State of California has proposed regulation according to the Proposition 65 list, by the Developmental and Reproductive Toxicant (DART) Identification Committee of the Office of Environmental Health Hazard Assessment (OEHHA). This was initially proposed of expedited review, which was changed in favour for an ordinary review. This proposal was based only on reproductive toxicity concerns (http://www.oehha.ca.gov/prop65/public_meetings/DART120402.html).

Table 7-1 Proposed EU Classification and Labelling for nPB

Classification	Label #	Warning	Text
	R10		Inflammable
Repr Cat 2:	R60		May impair fertility
Repr Cat 3:	R63		Possible risk of harm to the unborn child
Xn:	R48/20	Harmful:	Danger of serious damage to health by prolonged exposure through inhalation
Xi:	R36	Irritant:	Irritating to eyes
Xi:	R37	Irritant:	Irritating to respiratory system
Xi:	R38	Irritant:	Irritating to skin
	R67		Vapours may cause drowsiness and dizziness
	S2		Keep out of the reach of children
	S9		Keep container in well ventilated place
	S53-45		Avoid exposure – obtain special instructions before use - in case of accident or if you feel unwell, seek medical advice immediately

7.3 New Applications

No new applications have been reported in the past year.

7.4 New Production Facilities

New production facilities have gone on line in China. One facility, (a joint venture of Dead Sea Bromine Group and the Shandong Haihua Shareholding Co. Ltd., a subsidiary of the Shandong Ocean Chemical Group) started operation in late 2001, with reported new bromine production of 50,000 tonnes/year and with new capacity of 6,000 tonnes/year for nPB. The trading arm is Weifang City Sinobrom Economy Trading Co., Ltd (http://www.cnsinobrom.com), with offices in England. According to Internet information, the purity of the nPB offered from this plant meets all Western standards. E-mail publicity, from a different producer in China, claimed a

new production capacity of 12,000 tonnes of nPB/year but this has not been substantiated.

Two new distributors and blenders in the USA have been reported. Pacific Fluids (http://www.pacfluids.com/) in Tacoma, WA, have informed clients that they are now supplying nPB-based products. This company has published no information on their products on the Internet. Zep Manufacturing in Atlanta, GA, are providing an nPB-based solvent for wipe and spray applications (http://www.zepmfg.com/PSR/PSR_0555.pdf). The instruction sheet states "...may be used by spraying, immersion or wiping".

Actual production of nPB is estimated at 10,000 – 15,000 tonnes/year, of which about 5,000 tonnes is used by the pharmaceutical, agrochemical and speciality chemical industries (see 1.5 below). Total current production capacity of nPB is higher, conservatively estimated at more than 20,000 tonnes. If the demand exceeded this figure, more capacity could be brought on line.

7.5 Pharmaceutical, agrochemical and speciality chemical industries use of nPB

A considerable quantity of nPB is used as an "intermediate" substance for the manufacture of a wide range of products. If nPB were controlled under the Montreal Protocol, it is possible that most of these processes would fall into the definition of feedstock, but some may also be considered process agents. The direct and indirect emissions of nPB from these processes are unknown.

Pharmaceutical products concerned include: 5-Aminosalicylic acid (5-Amino-2-Hydroxybenzoic acid, 5-ASA, mesalazine, mesalamine); Oxibendazole; Sodium dipropylacetate (Dipropylacetic acid sodium salt, Sodium valproate, Valproic acid sodium salt, Sodium 2-propylvalerate, 2-Propylvaleric acid sodium salt); Albendazole; Probenecid Benemid; Ropivacaine; Propentofylline (3,7dihydro-3-methyl-1(5-oxohexyl)-7-propyl-1H-purine-2,6-dione); Albendazole oxide; Promestriene.

Agrochemicals include: Penconazole; Pirimiphos ethyl; Profenofos; Sulprofos.

Speciality chemicals include: Furfuryl propyl disulfide; 4-[[4-(1-Methylethoxy)phenyl]sulfonyl]phenol (4-(4-Isopropoxy-benzenesulfonyl)-phenol); Dipropylacetic acid (Valproic acid, 2-Propylvaleric acid, 2-Propylpentanoic acid); Prajmaline bitartrate; Dipropylacetamide; Sodium propyl thiosulfate.

The above lists are derived from information published on the Internet (http://www.chembourse.com/).

7.6 Ozone Depletion

At the time of writing, the SAP has not completed its studies. However, this Panel has published data indicating, "... the existing studies for nPB have shown that the ODP for a very short life source gas does vary with location and season of the emissions, by more than a factor of 5 for this particular gas, with the largest values for tropical emission." (UNEP, 2003) Table 2-12 in the same document cites one study giving the estimated ODP range over different large geographical ranges from 0.013 to 0.105, although "...there remain significant uncertainties in the existing studies".

7.7 Toxicity

The US National Institute for Occupational Safety and Health conducted a survey at a plant employing nPB-based adhesives (NIOSH, 2003). Average nPB exposure levels of the workers who were examined were 65.9 ppm. Participants most often reported headaches (48 percent), sleep problems (28 percent), dizziness or feeling "off balance" (25 percent), and blurred vision (24 percent). Blurred vision and dizziness were significantly more common among employees who worked with the adhesive than among employees who worked elsewhere in the plant. The employees experiencing symptoms had higher-than-normal levels of bromine compounds in their urine. NIOSH made recommendations to reduce worker respiratory and dermal exposure.

A useful summary of the known reproductive toxicity was drawn up for the public hearing of the DART Proposition 65 list in California, in 2002. (http://www.oehha.ca.gov/prop65/public_meetings/pdf/bromopropane120402.pdf).

7.8 Exposure Limits Recommended by Companies Marketing nPB

TEAP believes that no vendors of nPB solvents have changed their recommendations since the publication of the 2002 Update Report. There is still a wide range of maximum time-weighted-average operator exposure level from 5 ppm to 100 ppm. Most of the major manufacturers recommend 25 ppm[29], while some of the smaller blenders (who buy their nPB from the same major manufacturers) recommend 100 ppm. A new blender, Zep Manufacturing, recommends 25 ppm in their Material Safety Data Sheet (MSDS).

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[29] The US EPA also recommends 25 ppm, pending a definitive SNAP decision.

7.9 Ground water pollution

Suppliers of nPB claim that their solvents are less likely to cause ground water pollution than solvents like, trichloroethylene, because nPB is more subject to hydrolytic decomposition. However, nPB is more soluble in water (~2.5 g/l), which may contaminate aquifers.

7.10 Conclusions

i. The forecast global expansion of the nPB market has not yet occurred, because of the unclear regulatory situation, the current economic situation and geopolitical tensions.

ii. The bulk price of nPB, both raw and blended, has dropped to a level that is more competitive for general degreasing operations.

iii. The global production capacity of molecular nPB and blended solvents has expanded considerably and can meet foreseeable immediate demands if the regulatory and economic barriers are removed. Bromine production capacity is sufficient that more nPB can be produced at fairly short notice, if needed.

iv. nPB manufacturers and blenders are heavily promoting their products as replacements for non-ozone-depleting chlorinated solvents, exploiting possible regulatory loopholes.

v. The pharmaceutical, agrochemical and speciality chemical industries consume about 5,000 tonnes of nPB annually. The emissions from these are unknown.

vi. There is increased interest in the use of nPB in Article 5(1) countries, notably in the Peoples' Republic of China.

vii. Although there is no new information about the reproductive toxicity and neurotoxicity of nPB, there are grounds for concern arising from the incomplete toxicity or epidemiological information already available.

viii. Recommended safety practices regarding the use of nPB are not always being observed, resulting in excessive emissions and potential over-exposure of operators. In particular, more attention must be paid to the risks of dermal uptake, which may be more rapid in humans than was thought.

ix. In view of the still-unknown toxicology, epidemiology and risk to the ozone layer, the precautionary principle could discourage use of nPB in emissive solvents applications, and could require that every

measure be taken to protect the operators from risk of exposure and to minimise emissions.

7.11 References

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Rollet 2003: E-mail (translated from French) sent to Brian Ellis, 18 March 03

TEAP 2002: Report of the Technology and Economic Assessment Panel, April 2002, ISBN 92-807-2227-1, UNEP Ozone Secretariat, Nairobi, Kenya

UNEP 2003: 2002 Assessment Report of the Science Assessment Panel, 2003, UNEP Ozone Secretariat, Nairobi, Kenya